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The Electron — Water Vapor (H_2O) Collision Cross Sections

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Plasma Physics Division

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A set for electron-H_2O collision cross sections is developed over a wide range of electron energies. The set comprises the total, ionization, dissociative ionization, dissociative excitation, electronic, vibrational, rotational, elastic, and momentum transfer cross sections.

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THE ELECTRON—WATER VAPOR (H_2O) COLLISION CROSS SECTIONS

1. INTRODUCTION

Water vapor (H_2O) is one of the minor constituents of the atmosphere and it plays an important role in the deionization processes of the partially ionized air. It controls the air conductivity, especially that of the unheated air. Therefore, the role of H_2O in modifying the electron velocity distribution in wet air is required for characterizations of partially ionized wet air. This requires the solution of a Boltzmann equation with an appropriate set of electron-molecule scattering cross sections.

This report, accordingly, presents a set of up to date cross sections for the electron - H_2O collisions over a wide range of electron energies.

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2.0 THE IONIZATION OF H_2O

The electron impact ionization of H_2O results in the ionization of H_2O as well as in several dissociative ionization channels. These are:

$$e + H_2O \rightarrow H_2O^+ + 2e \quad (1)$$

$$e + H_2O \rightarrow OH^+ + H + 2e \quad (2)$$

$$e + H_2O \rightarrow O^+ + H_2 + 2e \quad (3)$$

$$e + H_2O \rightarrow H^+_2 + O + 2e \quad (4)$$

$$e + H_2O \rightarrow H^+ + OH + 2e \quad (5)$$

One of the very early measurements by Mann, et al[1], in 1940, of the H_2O ionization cross sections, gave only the relative ion abundancies generated by electrons with energy of 100 eV. These values were 100, 23.2, 2.0, 0.07 and 5.0 for the relative productions of H_2O^+, OH^+, O^+, and H^+_2 and H^+, respectively. However, the measurements of Schutten, et al[2], some 26 years later provided partial ionization cross sections for the above processes for electron energies from 20 to 1000 eV. It also provided the relative abundancies of the ions produced by the impact of electrons with energy of 100 eV.

These are 100, 25.8, 2.65, 0.3 and 29.6 for H_2O^+, OH^+, O^+, H_2^+ and H^+, respectively. These results differ sharply from those of Mann et al[1], especially for the productions of H_2^+ and H^+. The total and partial ionization cross sections of H_2O are shown in Fig. 1 and are also given in Table 1, based on data from Ref. 2, where it is obvious that the dominant contributions to the total ionization are from H_2O^+, OH^+ and H^+. These values are from threshold energies to 1000 eV; however, for higher impact energies, the ionization cross section can be obtained by using the following equation[3].

$$\sigma_i = A_i \frac{4\pi a_o^2 R^2}{I_i E'} \left[\log \frac{4C_i E'}{I_i} (1-\beta^2) - \beta^2\right] \qquad (6)$$

where $E' = \frac{1}{2} mc^2\beta^2$, A_i and C_i are adjustable parameters, a_o is the Bohr radius and R is the Rydbeg constant (13.6 eV).

3. THE DISSOCIATION OF H_2O

The dissociation of H_2O has many channels. These are:

$$e + H_2O \rightarrow OH + H + e \qquad (7)$$

$$e + H_2O \rightarrow H_2 + O + e \qquad (8)$$

$$e + H_2O \rightarrow H + H + O + e \qquad (9)$$

No absolute measurements of these cross sections exist. However, absolute emission cross sections for the dissociative excitation

processes have been measured. These dissociative excitations are; the OH ($A^2\Sigma$) excitation which emits radiation in the 2810 - 3500Å, the Lα, Hα, Hβ, Hγ and Hδ emissions from the hydrogen atom and the 1302Å, 7774 Å and 8447Å emissions from the oxygen atom. The emission cross sections of OH ($A^2\Sigma$), Hβ, O(8447Å) and O(7774Å) have been measured by Beenakker, et al[4], in the energy range of 20 - 1000 eV. Furthermore, the emission cross sections for Hα, Hγ, and Hσ have been measured at 300 eV and are normalized to that of Hβ. The measurements of these emissions at 100, 200, 500 and 800 eV indicate[4] the same energy dependence, as that of Hβ.

TABLE I

TOTAL AND PARTIAL IONIZATION CROSS SECTIONS

ENERGY (eV)	H_2O^+	OH^+	O^+	O^{++}	H_2^+	H^+	TOTAL
20	4.2(-17)*	3.0(-18)	9.0(-20)		1.8(-19)	7.0(-19)	4.6(-17)
30	7.6(-17)	1.3(-17)	3.7(-19)		2.2(-19)	7.8(-18)	9.7(17)
50	1.07(-16)	2.4(-17)	1.7(-18)		3.0(-19)	2.4(-17)	1.57(-16)
100	1.32(-16)	3.4(-17)	3.5(-18)		3.9(-19)	3.9(-17)	2.10(-16)
150	1.16(-16)	3.1(-17)	3.6(-18)	6.0(-20)	3.6(-19)	3.7(-17)	1.89(-16)
200	1.08(-16)	2.8(-17)	3.5(-18)	1.4(-19)	2.8(-19)	3.6(-17)	1.75(-16)
500	6.4(-17)	1.7(-17)	1.9(-18)	1.3(-19)	1.8(-19)	2.3(-17)	1.06(-16)
700	5.0(-17)	1.4(-17)	1.4(-18)	9.0(-20)	1.6(-19)	1.7(-17)	8.3(-17)
1000	4.1(-17)	1.1(-17)	1.1(-18)	6.0(-20)	8.0(-20)	1.3(-17)	6.5(-17)
1500	2.9(-17)	8.0(-18)	8.0(-19)			1.1(-17)	4.9(-17)
2000	2.3(-17)	6.0(-18)	6.0(-19)			8.0(-18)	3.7(-17)

*4.2(-17) implies 4.2 x $10^{-17}cm^2$

These cross sections, based on the measurements of Beenakker, et al[4], are given in Table II and are shown in Figure 2. The excitation of the 1304Å line of oxygen from the dissocation product has been measured by Lawrence[5] and the absolute emission cross section of Lγ has been measured by Vroom and de Heer[6]. The data for the last two cross sections is given in Table III and are also shown in Fig. 2.

4. THE EXCITATION OF H_2O

4.1 The Electronic Excitations

There exist no measured cross sections for the electronic excitations for H_2O. However, high energy electron scattering spectra have been obtained by Lassettre and co-worker[7-10]. The generalized oscillator strengths obtained by these workers can be utilized[11] to obtain the excitation cross sections through the appropriate relations, especially for the optically allowed transitions. Trajmar, et al,[12,13], have detected two excitations in H_2O at 4.5 and 9.8 eV with features appropriate to triplet - singlet transitions. However, to date, theoretical calculations (See Ref. 13, 14) indicate no electronic excitations for states below 6 eV. Yousfi, et al[14], give the cross sections for two H_2O excitations with thresholds at 7.5 and 11.8 eV. These cross sections are shown in Figure 3 and are also given in Table IV.

TABLE II

EMISSION CROSS SECTIONS IN UNITS OF 10^{-19}cm^2

Energy (eV)	$OH(A^2\Sigma)$	$H\alpha$	$H\beta$	$H\sigma$	$H\delta$	0 8447Å	0 7774Å
40	66.3	15.82	3.06	1.132	0.428	1.40	0.95
50	60.3	20.88	4.04	1.49	0.56	1.88	1.16
60	56.6	27.14	5.25	1.94	0.73	2.30	1.29
70	53.5	30.45	5.89	2.18	0.82	2.54	1.33
80	50.8	32.31	6.25	2.31	0.87	2.70	1.32
90	48.3	33.09	6.4	2.37	0.89	2.8	1.28
100	46.4	33.14	6.41	2.37	0.89	2.86	1.26
120	43.2	31.69	6.13	2.27	0.86	2.87	1.17
140	40.0	30.14	5.83	2.16	0.82	2.59	1.02
170	36.4	26.98	5.22	1.93	0.73	2.53	0.80
200	33.9	25.13	4.86	1.79	0.68	2.32	0.73
250	29.7	21.61	4.18	1.55	0.58	1.9	0.54
300	26.6	19.02	3.68	1.36	0.51	1.67	0.46
400	22.4	15.09	2.92	1.08	0.41	1.30	0.36
450	20.6	13.54	2.62	0.97	0.36	1.13	0.35
500	19.6	12.35	2.39	0.88	0.33	1.05	0.28
600	17.9	10.59	2.05	0.76	0.28	0.89	0.24
700	15.8	9.41	1.82	0.67	0.25	0.78	0.17
800	14.9	8.32	1.61	0.59	0.22	0.68	0.17
900	13.1	7.6	1.47	0.54	0.20	0.58	0.16
1000	12.1	7.13	1.38	0.51	0.19	0.53	0.14

TABLE III

EMISSION CROSS SECTIONS

Energy (eV)	L_γ	1304Å
40		1.3(-19)
50	2.54(-17)	2.8(-19)
60	2.60(-17)	3.3(-19)
80	2.61(-17)	3.7(-19)
100	2.58(-17)	3.7(-19)
150	2.14(-17)	2.7(-19)
200	1.87(-17)	2.3(-19)

TABLE IV

EXCITATION CROSS SECTIONS OF H_2O

E(ev)	Eth=7.1 eV	Eth=11.8 eV
7.1	0	
11.8	0	
15	0.12(-16)	
16		0.078(-16)
20	0.2(-16)	0.135(-16)
30	0.27(-16)	0.180(-16)
40	0.32(-16)	0.213(-16)
55	0.33(-16)	0.225(-16)
80	0.30(-16)	0.202(-16)
100	0.25(-16)	0.168(-16)
120	0.20(-16)	0.135(-16)
140	0.15(-16)	0.101(-16)
180	0.12(-16)	0.078(-16)
260	0.07(-16)	0.045(-16)
320	0.033(-16)	0.022(-16)
400	0.017(-16)	0.011(-16)

4.2 The Vibrational Cross Sections

The vibrational excitation of H_2O consists of the stretching modes ν_1, ν_3, the bending mode ν_2, their harmonics and sums of these frequencies (see e.g. Ref. 10). However, the emission measurements of Ref. 10 and the most recent cross section measurements[15,16], indicate that ν_1, ν_2, and ν_3 are the strongest vibrational transitions in H_2O. Furthermore, ν_1 and ν_3 are blended together and are not separated experimentally. The cross section for ν_2 and (ν_1,ν_3) based on measurements of Rhor[15] and Seng and Linder[16] are shown in Fig. 4 and are also given in Table V.

4.3 The Rotational Cross Sections

Experimental data on the rotational excitation of H_2O is limited[17] to the differential scattering cross sections at impact energies of 2.4 and 6.0 eV. These measurements by Jung, et al[17], are for the excitation and de-excitation processes ($\Delta j=\pm1$). Jung, et al[17], have also measured the differential cross sections for the elastic process at the two energies mentioned earlier.

These differential cross sections have been integrated by Danjo and Nishimura[18] to provide the total elastic scattering cross section at 2.14 and 6.0 eV. These values are in good agreement with the total elastic scattering cross section measured by Danjo and Nishimura[18]. This provides reasonable confidence in the magnitude of the differential cross sections for rotational excitation . Furthermore, Jain and Thompson[19] have calculated the rotational excitations of H_2O in the range of 1 - 10 eV. The calculated differential cross sections, however, are at least a factor of 3 larger in comparison with the measured values of Jung, et al[17], at 2.14 and 6.0 eV. These results are shown in Figure 5 along with the proposed rotational cross section by Yousfi, et al[14], based on swarm data and solution of the Boltzmann equation.

TABLE V

VIBRATIONAL CROSS SECTION OF H_2O

Energy (eV)	(ν_1, ν_3)	(ν_2)
0.2	0	0
0.3	2.0(-19)	3.0(-17)
0.4	3.0(-18)	9.5(-17)
0.5	3.0(-17)	6.0(-17)
0.6	1.4(-16)	4.5(-17)
0.7	2.0(-16)	3.0(-17)
0.8	1.35(-16)	2.5(-17)
0.9	9.5(-17)	1.7(-17)
1.0	7.0(-17)	1.35(-17)
1.5	1.95(-17)	7.5(-18)
1.6	1.75(-17)	7.55-18)
1.8	1.75(-17)	8.0(-18)
2.0	1.95(-17)	8.5(-18)
2.2	2.05(-17)	9.0(-18)
2.4	2.15(-17)	9.5(-18)
2.6	2.20(-17)	1.0(-17)
2.8	2.30(-17)	1.05(-17)
3.0	2.35(-17)	1.1(-17)
3.5	2.45(-17)	1.25(-17)
4.0	2.60(-17)	1.3(-17)
5.0	2.80(-17)	1.4(17)
6.0	3.00(-17)	1.5(-17)
7.0	3.00(-17)	1.5(-17)
8.0	3.00(-17)	1.4(-17)
9.0	2.60(-17)	1.2(-17)
10	2.10(-17)	9.5(-18)

5. THE TOTAL, ELASTIC AND MOMENTUM TRANSFER CROSS SECTIONS

5.1 The Total Scattering Cross Section

The total scattering cross section of electrons in H_2O has been measured from 0.5 to 1000 eV. The earliest measurement is that of Brüche[20] (1929) for impact energies of 1.5 to 40 eV. The other measurements are very recent and have been carried out from 1981 to 1987. These are: Sokolov[21] (1981) in the energy range of 0.5 - 7 eV, Sueoka, et al[22], (1986) from 1.0 to 80 eV, Szmytkowski, et al[23], and Szmytkowski[24] (1987) in the energy range of 0.5 - 1000 eV, and those of Seng and Linder (See Ref. 23) from 0.5 - 10 eV. These measurements are shown in Figure (6) and are given in Table (VI)

5.2 The Elastic Cross Section

The electron elastic scattering cross section in H_2O has been measured by Danjo, et al[18], in the range of 4 to 200 eV and by Katase, et al[25], in the range of 100 - 1000 eV. These measured values are shown in Figure (7) along with the total scattering cross section of Szmytkowski[23]. The numerical values of these elastic cross sections are given in Table (VIIA).

TABLE VI

TOTAL SCATTERING CROSS SECTION IN ($10^{-16}cm^2$)

Energy (eV)	SZ	B	SL	SO	SU
0.01				3000	
0.02				2000	
0.04				1500	
0.06				1100	
0.08				800	
0.1				600	
0.5	70.2		81.1	125	
0.7	52.8			87	
1.0	40.2		37.0	60	29.2
1.5	28.8	23.1		40	
2	24.0	20.2	19.4	30	15.8
3	20.7	17.2	15.3	20	
4	19.5	16.1	13.9	16	12.2
5	19.8	16.3	14.2	13.3	11.9
6	20.0	16.5	15.3	11.8	12.5
7	20.7	16.8	16.7	10.8	12.6
8	20.9	17.4	17.7		13.0
9	21.1	17.8	18.1		13.2
10	20.9	18.1	18.1		12.7
12	19.0	18.2			12.8

TABLE VI

TOTAL SCATTERING CROSS SECTION IN ($10^{-16}cm^2$)
(Continued)

Energy (eV)	SZ	B	SL	SO	SU
16	16.7	16.7			12.0
20	15.7	15.0			11.3
25	14.1	13.3			10.2
30	12.7	11.9			9.5
35	11.8	10.8			9.0
40	11.0	10			8.5
50	9.7				7.5
60	8.2				7.1
70	8.1				6.7
80	7.5				6.3
100	6.65				
200	4.50				
300	3.5				
400	2.80				
500	2.50				
1000	1.43				

Symbols:
B = Ref 20
SL = See Ref 24
SO = Ref 21
SU = Ref 22
SZ = Refs 21 and 24

TABLE VIIA

ELASTIC AND MOMENTUM TRANSFER CROSS SECTIONS

Energy (eV)	σ_e(D)	σ_m(D)	σ_e(K)	σ_m(K)
4	1.04(-15)	6.18(-16)		
5	1.05(-15)	6.17(-16)		
6	1.06(-15)	6.40(-16)		
8	1.11(-15)	6.43(-16)		
10	1.2(-15)	6.81(-16)		
15	9.93(-16)	5.74(-16)		
20	8.21(-16)	4.37(-16)		
30	5.72(-16)	2.65(-16)		
40	4.68(-16)	2.34(-16)		
50	3.97(-16)	1.65(-16)		
60	3.34(-16)	1.37(-16)		
80	2.63(-16)	8.86(-17)		
100	2.37(-16)	8.62(-17)	2.98(-16)	1.01(-16)
150	1.78(-16)	5.26(-17)		
200	1.50(-16)	5.04(-17)	2.11(-16)	0.464(-16)
300			1.56(-16)	0.296(-16)
400			1.32(-16)	0.208(-16)
500			1.04(-16)	0.156(-16)
700			0.819(-16)	0.093(-16)
1000			0.548(-16)	0.0515(-16)

σ(D) = Ref 18
σ(K) = Ref 25

5.3 The Momentum Transfer Cross Section

The electron momentum transfer cross section in H_2O has been measured by Danjo, et al[18], in the energy range of 4.0 to 200 eV, and by Katase, et al[25], in the energy range of 100 to 1000 eV. These values are given in Table (VIIA). Furthermore, Pack, et al[26], have obtained the momentum transfer cross in H_2O for very low electron energies, i.e., for 0.003 to 0.08 eV through swarm data analysis. They give the following expression for the momentum transfer cross section, where E is

$$\sigma_m = 10^{-14} \left[2.74E + 2.54(E)^{3/2}\right]^{-1} \qquad (10)$$

the electron energy in eV. Using Eq. (10) the numerical values of the cross section are given in Table VIIB along with data from Itikawa's compilation[27].

6. THE DISSOCIATIVE ATTACHMENT CROSS SECTION

Electron collisions with H_2O lead to the generation of negative ions in addition to all other processes discussed earlier. The negative ions are H and O and are produced by the process of the dissociative attachment.

$$e + H_2O \rightarrow \bar{H} + OH \qquad (11)$$

$$e + H_2O \rightarrow \bar{O} + H_2O \qquad (12)$$

TABLE VIIB

MOMENTUM TRANSFER CROSS SECTION (cm^2)

ELECTRON ENERGY (eV)	P	ELECTRON ENERGY (eV)	I
0.01	3.34(-13)	0.5	3.5(-15)
0.02	1.61(-13)	0.8	2.0(-15)
0.04	7.69(-14)	1.0	1.5(-15)
0.06	4.96(-14)	2.0	6.0(-15)
0.08	3.61(-14)	[illegible].0	5.5(-15)
0.1	2.82(-14)	4.0	6.0(-15)
		5.0	6.8(-15)
		6.0	7.7(-15)
		7.0	7.9(-15)
		8.0	8.0(-15)
		10	7.5(-15)

Symbols:
P = Ref 26
I = Ref 27

Where the cross section for process (11) has been measured by Crompton and Christophorou[28] and Belic et al[29]. The relative strength of process (12) is indicated[28] to be one order of magnitude smaller than that of process (11). These cross sections are given in Table VIII. The onsets of process (11) and (12) occur at 5.7 and 7.5 eV and the peak of their cross sections are at 6.5 and 11.5 eV. respectively. Process (12), on the other hand, has two[28] other peaks which are at 7 and 9 eV. These measurements have been made at low gas pressures, however, at higher pressures one observes OH formation which is due to ion-molecular reactions. One of the interesting observations of the H formation in process (11) is that OH is vibrationally excited[29]. Belic, et al[28] have observed excited vibrational levels up to v = 7 and have resolved the excitations of individual levels as a function of the electron energy.

TABLE VIII

THE DISSOCIATIVE ATTACHMENT CROSS SECTION

Electron Energy (eV)	H (Ref 28)	Electron Energy (eV)	H (Ref 27)	Electron Energy (eV)	O (Ref 27)
5.56	0.9(-18)	5.6	0	5	0
5.87	2.0(-18)	6.0	2.5(-18)	6	3.9(-20)
6.0	3.0(-18)	6.5	6.9(-18)	7	1.6(-19)
6.25	5.0(-18)	7.0	4.3(-18)	8	3.9(-20)
6.5	6.4(-18)	7.5	1.6(-18)	9	3.90(-19)
6.75	5.2(-18)	8.0	1.2(-18)	10	2.7(-19)
7.0	3.8(-18)	8.5	1.25(-18)	11	6.3(-19)
7.25	2.5(-18)	9.0	1.0(-18)	11.5	6.9(-19)
7.5	1.2(-18)	9.5	0.5(-18)	12	5.5(-19)
7.7	0.8(-18)	10.0	0.3(-18)	13	1.8(-19)
		11	0.2(-18)	14	7.0(-20)
				15	2.3(-20)

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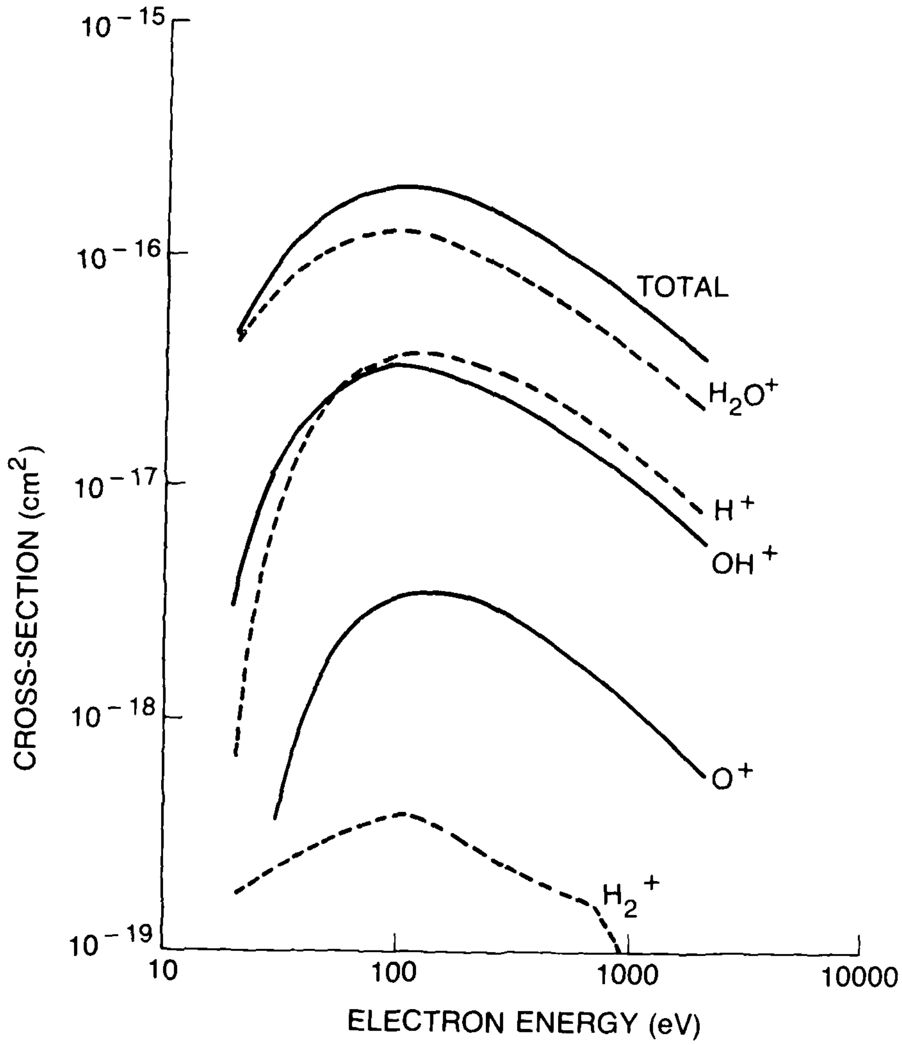

Figure 1 Total and Partial Ionization Cross Sections of H_2O

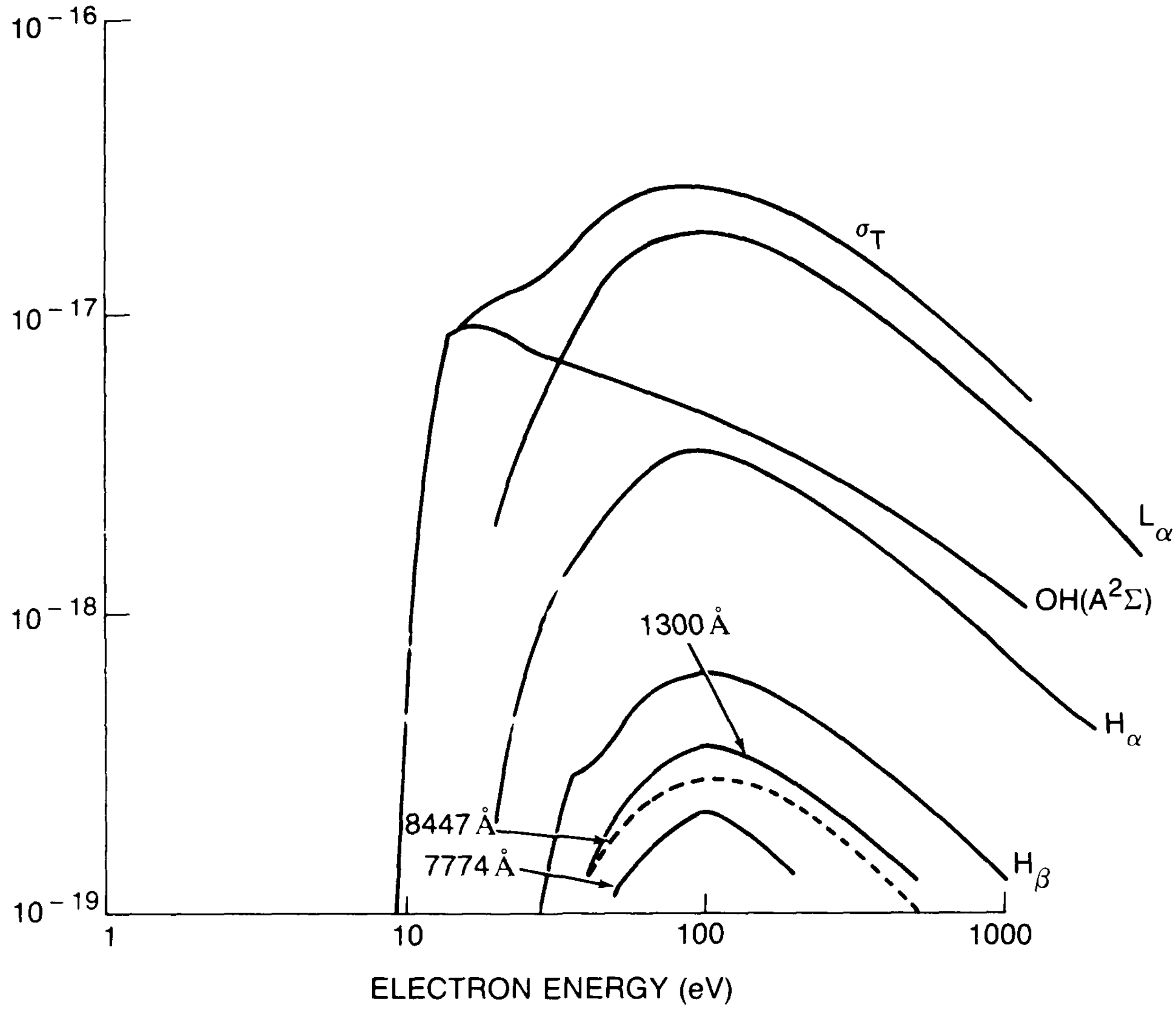

Figure 2 Emission Excitation Cross Sections of Dissociative Excitations Products of H_2O and their Sum (σ_T)

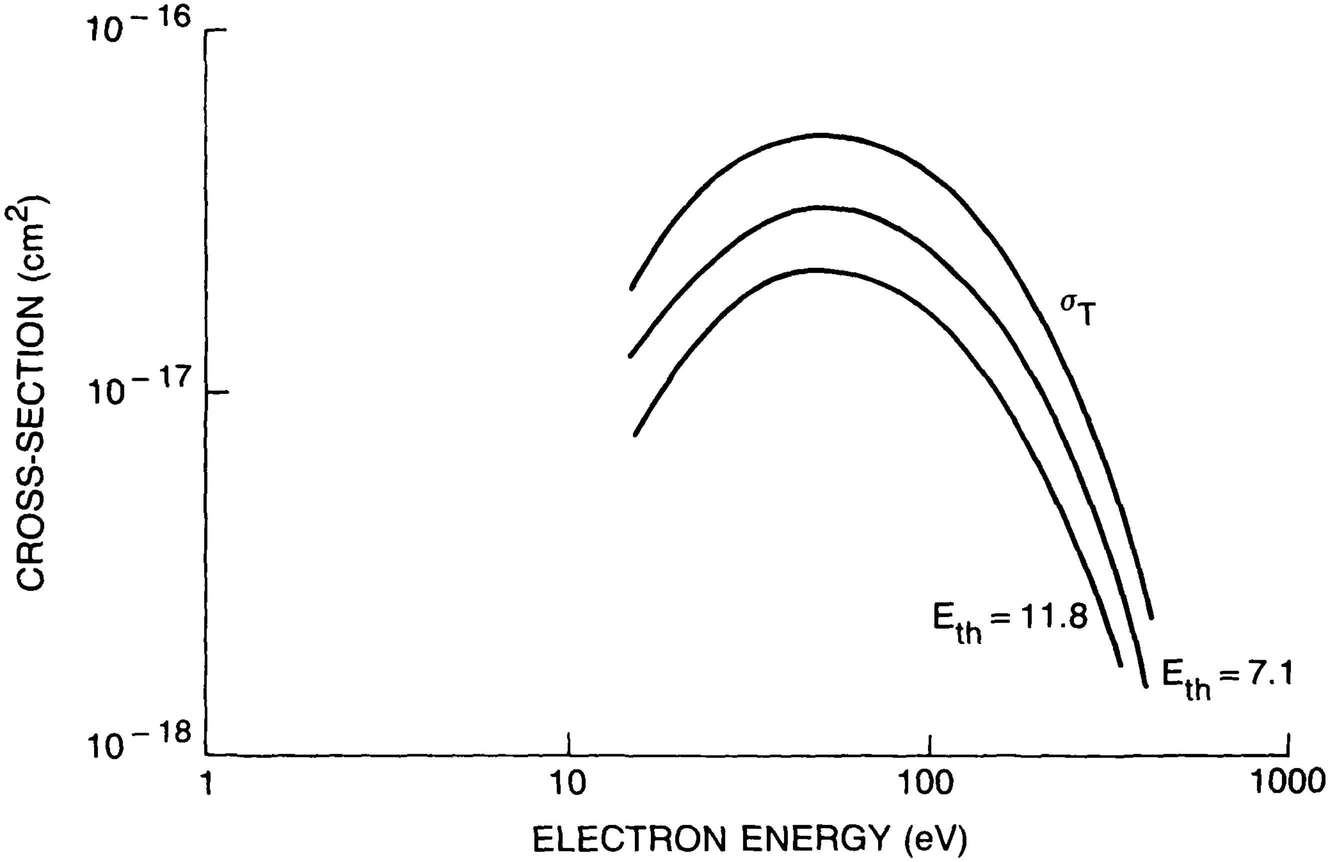

Figure 3 Excitation Cross Sections of Two Electronic States in H_2O and their sum (σ_T)

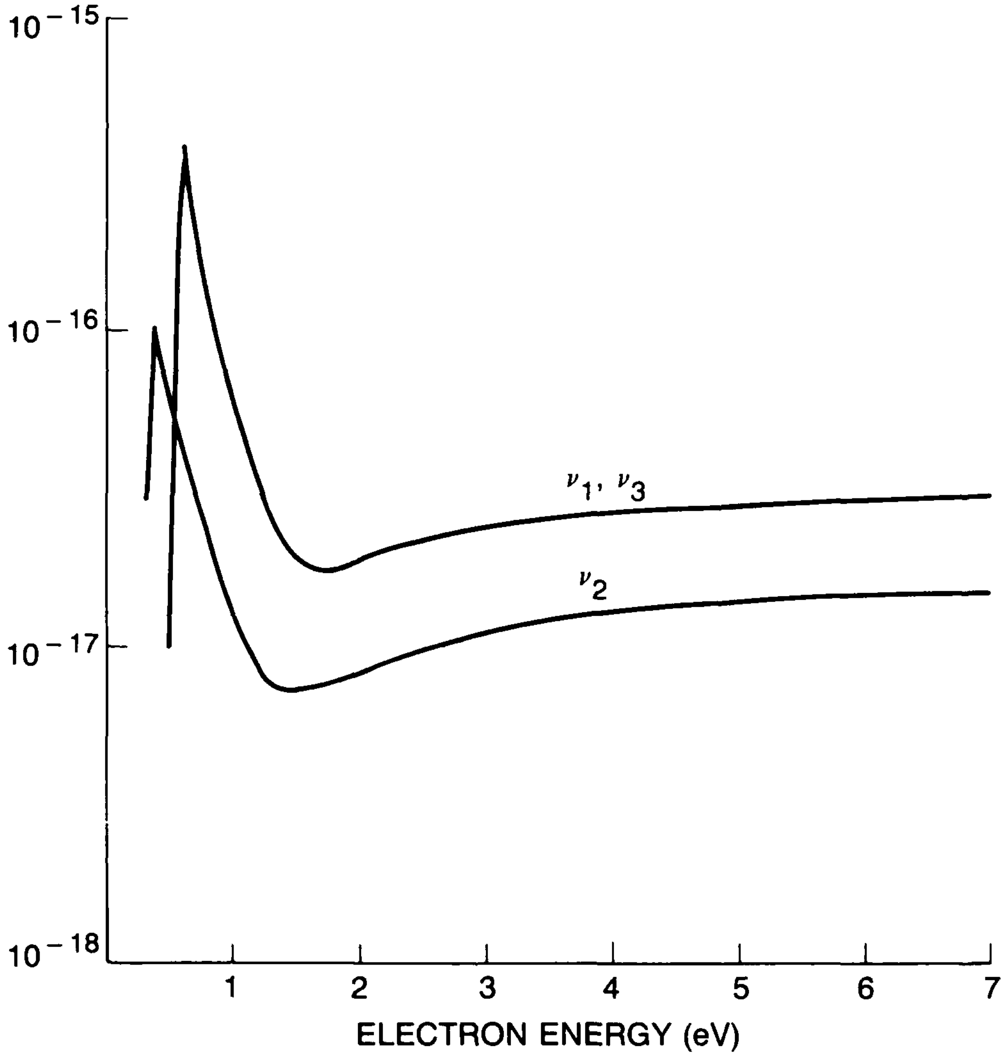

Figure 4 Excitation Cross Sections of the H_2O Vibrational Levels

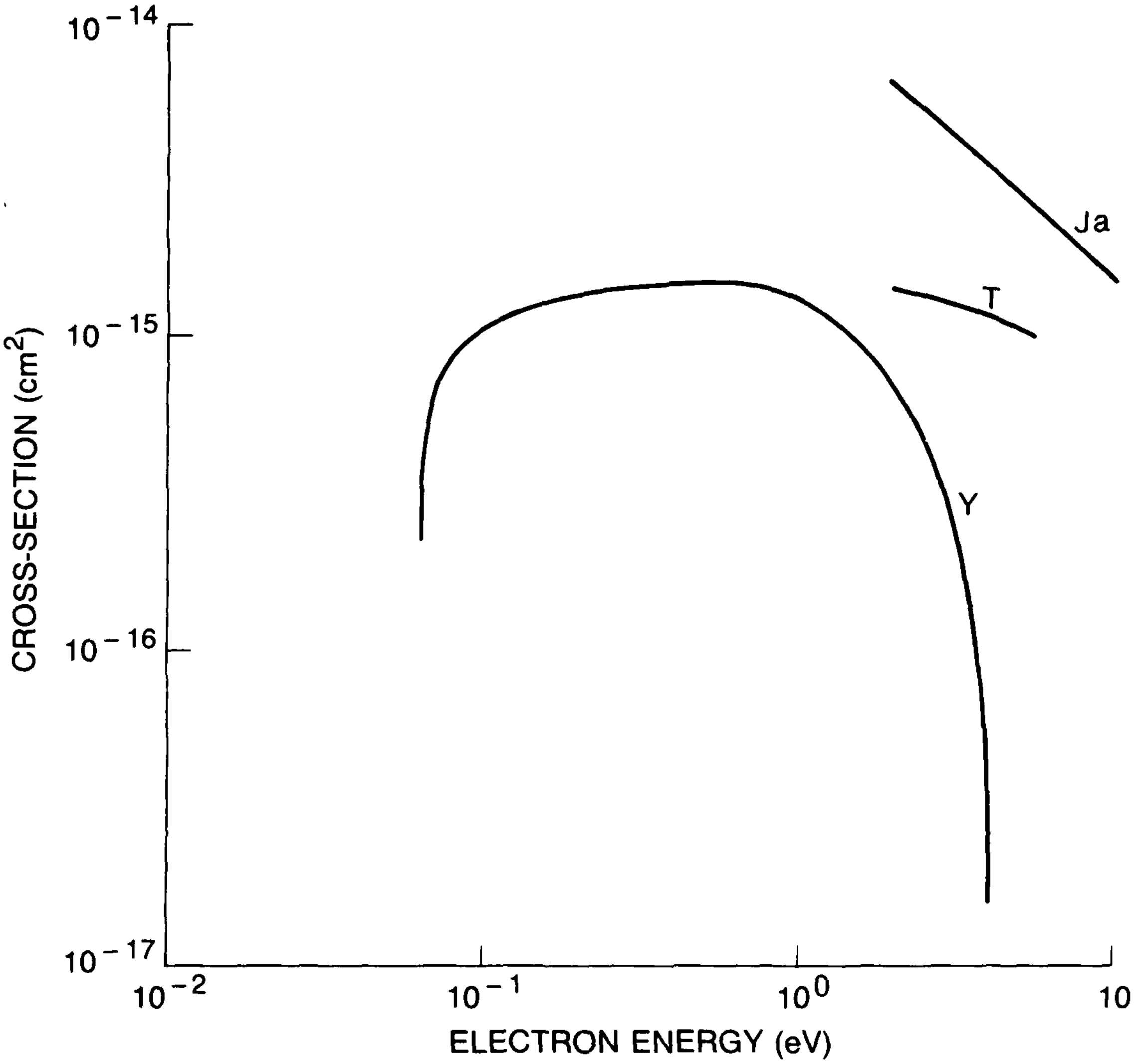

Figure 5 Rotational Excitation Cross Section of H_2O

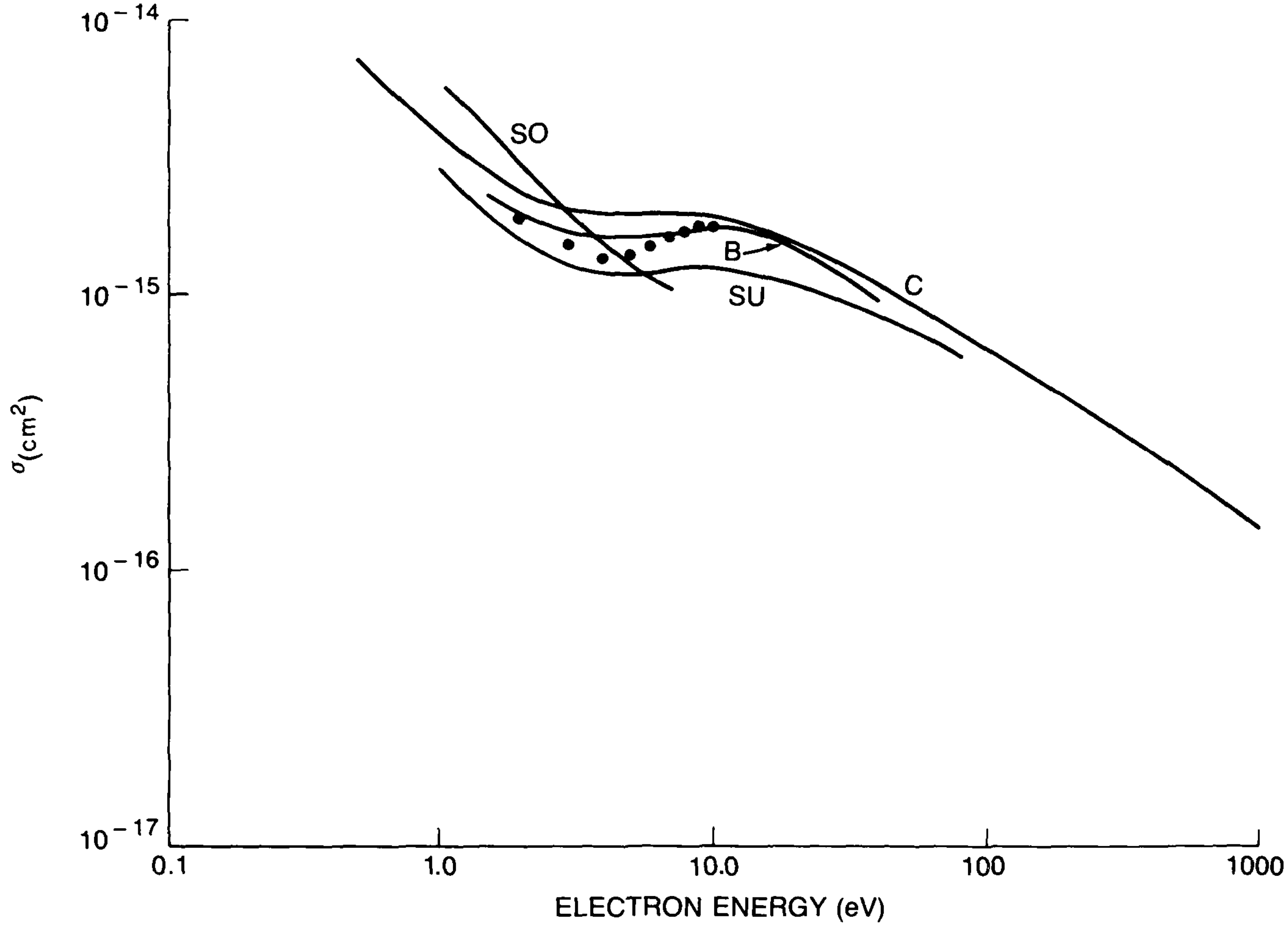

Figure 6 Total Scattering Cross Section in H_2O

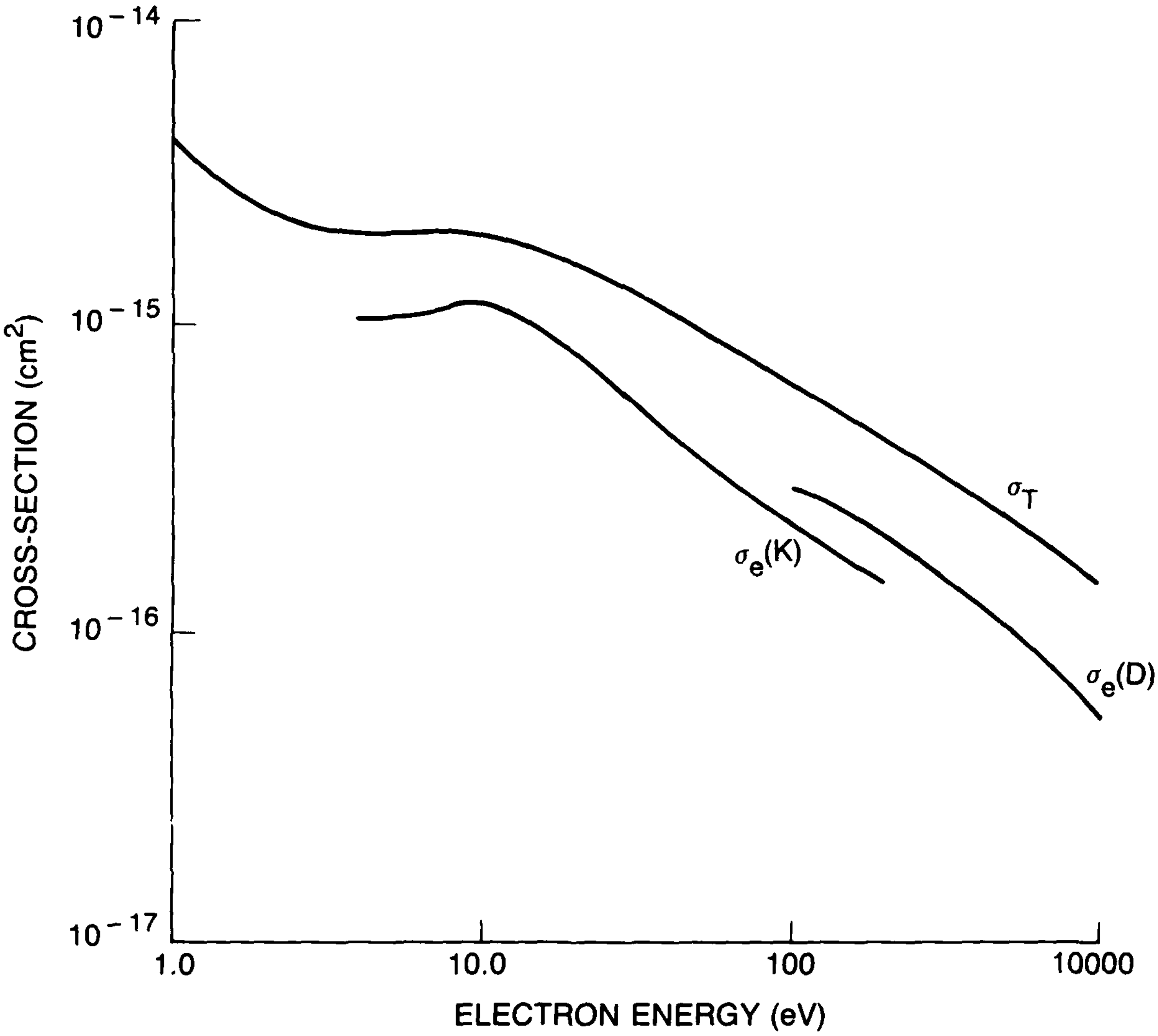

Figure 7 Elastic Scattering Cross Section in H_2O shown along with the Total Scattering Cross Section

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